Development of Reference Materials for Atmospheric Analysis of the Occupational Environment: Filter Samples Containing Toxic Metals

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Department of Commerce
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ABSTRACT

Techniques are described that may be used to prepare
filters on which are deposited prescribed amounts of heavy
metals, for use as reference materials in industrial
atmospheric analysis. Working solutions, prepared from pure
metals and highly purified acids and water, are pipetted
onto the filters held in jigs to facilitate their application.
The techniques were used to prepare three sets of reference
materials containing the following metals: Set 1--Pb, Cd, Zn,
Sn; Set 2--Pb, Zn, Mn; Set 3--Be. The amounts of each
metal deposited on the filters correspond to those expected
when collecting personal samples, in atmospheres when the
concentrations are both below and above the TLV levels.

1. INTRODUCTION

This report describes work performed by the National

Bureau of Standards for the National Institute of Occupational

Safety and Health under an Interagency Agreement, to develop

analytical reference standards related to atmospheric analysis

of the occupational environment. The objective was to develop

techniques for preparation of materials suitable for service

as reference materials, and also to produce an initial lot

of such materials for NIOSH use in method evaluation. The

materials are required to simulate field samples with respect

to the critical steps in a given determination and to be

specifically applicable to NIOSH recommended methodology.

The determination of toxic metals in the industrial

atmosphere is becoming increasingly important. Such

substances enter the atmosphere as dust, fumes, and sprays, for

example, and need to be monitored to ascertain that safe levels have not been exceeded. It is obvious that the methodology used for such monitoring be reliable and that the measurements be made with adequate quality control.

This report describes the development of techniques for preparing filters, such as used in atmospheric sampling, containing specified amounts of several of the more important toxic metals. The combinations selected are typical of those found in metal industry atmospheres and the amounts simulate the amount that might be collected on a personal sampling monitor during an 8 hour day, for air concentrations both below and above the TLV levels.

2. EXPERIMENTAL

2.1 Materials Used

Substrate: Membrane filters, type MF-HA (mixed esters of cellulose) 47 mm diameter, mean pore size 0.45 μm, white, plain. Plastic petri dishes to serve as containers for the filters. Filter holders: Made of cylindrical Plexiglass, 50 mm o.d.; 40 mm i.d., 60 mm high, and provided at the top with a groove to center the filter and a side notch to facilitate removal of the filter by means of tweezers (Fig. 1). Twelve of these filter holders were made and used throughout this work. V-block: Made of plexiglass, 60 mm long, 50 mm wide, 25 mm thick, provided with a 90° V cut. This block is fastened to a labora-

tory stand by means of a metal rod attached at the rear of the block. It is used to center the filter in its cylindrical holder under the micro-pipette tip (Fig. 1).

Micro-pipette Push-button type microliter pipette, capacity 0.1 ml. The pipette is secured to the stand with two clamps, and is positioned with the plastic tip at the center of the membrane filter holder and 2 mm above the filter (Fig. 1).

2.2 Solutions

The acids used in preparing the solutions and the water used for dilutions were prepared in the Analytical Chemistry Division by the methods described in Reference [1]. Stock solutions of Pb, Zn, Mn, Cd and Be were prepared by dissolving the pure metal (at least 99.9 percent) in 1000 ml of NBS high purity HNO_3-H_2O (NBS non-ebullient). NBS high purity HCl was used to dissolve the tin.

The following weights were taken for each metal: Pb = 3.0000 g; Zn = 40,001 g; Mn = 100.001 g; Cd = 2.0001 g; Be = 40.00 mg; Sn = 60.00 g. Suitable dilutions were made with NBS non-ebullient distilled water to produce working solutions for filter preparation. The composite solutions for filter Series No. 1 were made containing Pb, Cd, and Zn. Because Sn was not compatible in the composite solution, a dilute single element solution was used in the second step of the filter preparation. The composite solutions for filter Series No. 2 contained Pb, Zn, and Mn. The solutions for filter Series No. 3 contained only Be. The composite solutions were prepared to contain the following metals:

3

<u>Metal, µg/0.1 ml</u>

Series No.1	Pb	Cd	Zn	Sn	Mn	Be
1A	7.5	5	100	150	--	--
1B	15	10	200	300	--	--
1C	30	20	400	600	--	--
Series No. 2						
2A	7.5	--	100	--	250	--
2B	15	--	200	--	500	--
2C	30	--	400	--	1000	--
Series No. 3						
3A	--	--	--	--	--	0.1
3B	--	--	--	--	--	0.2
3C	--	--	--	--	--	0.4

A 0.1 ml volume of these solutions was used to transfer the metals on each membrane filter.

All stock solutions were kept in 1000-ml polyethylene bottles and special dispensing bottles of 250 ml capacity were used for the composite solutions (Fig. 1).

All pipetting, transfer, and filter drying operations were performed in a polypropylene laminar flow hood (Fig. 1).

3. Preparation of the Membrane Filters with Deposited Metals

3.1 Filter Capacity

The capacity of a membrane filter to accept a given volume of solution is a function of its size and absorption character-

istics. This capacity was determined for the material used in this work and was found to be approximately 0.1 ml. When this volume was applied by the micro-pipette to the center of the filter, held on the plexiglass support, a spot was obtained which covered no more than 75 percent of the surface of the filter; this spot did not reach the edges of the filter. Under this condition there was no danger of losing the material applied to the filter, hence the volume of 0.1 ml was used in the work reported here.

3.2 Accuracy of Micro-Pipettes

The accuracy and precision of the micro-pipettes used were determined by weighing the pipetted nominal volume of 0.1 ml of distilled water using a microbalance. Three pipettes were tested by 20 individual weighings of the water delivered in a pipetting operation. In each case, the relative standard deviation of 0.5 percent showed the excellent reproducibility that can be achieved. The three pipettes delivered less than the nominal amounts, with negative biases of -1.5, -1.3 and -1.1 percent respectively. The last one was used in all of the preparations described later.

3.3 Transfer of Metal Solutions to the Filters

3.3.1 Filter Identification

Each filter was identified by inscribing at the edge the corresponding group member (e.g. for Series 1 dilution A, B, and C = 1A; 1B; 1C, and B1 for blank). An aqueous solution of nigrosin was used to write these numbers using a conventional pen. Before the analysis, the numbers were removed by cutting a correspond-

ing small portion of the edge of the filter with small scissors to avoid any interferences of the ink dye with the analytical procedure used. The same procedure should be used previous to the analysis of all of the filters.

3.3.2 Transfer Operation

This operation, which is illustrated in Figure 1, was performed in an all-polypropylene hood with vertical laminar flow provided with clean air filters.

A filter was placed on each of the 12 plexiglass filter holders using flat-tip tweezers. The polyethylene dispensing bottle containing the appropriate solution, was placed under the micro-pipette and the volume of 0.1 ml was withdrawn into the plastic tip. A filter holder was placed in the V block to facilitate centering and locating the filter under the pipette tip at a distance of about 2 mm. The pipette was then operated and the solution was transferred to the filter. The filter in its holder was then kept in the hood until the solution had completely evaporated (15 minutes). The dried filter was then placed in the corresponding plastic petri dish container. Each container includes two blank filters followed by two filters for each of the three levels produced, bringing the total number of filters in the container to 8. Each filter was separated from the others using the spacers provided initially by the manufacturer.

For preparation of Series No. 1 filters, two transfer operations were required because of the incompatibility problem

of the working solution, already mentioned. In all other cases,
a single transfer operation was possible.

4. Analysis of the Filters

The following procedures were used to analyze the filters
to verify the content of the added metals: flame atomic absorp-
tion for Pb, Zn, Cd, and Mn; spectrophotometry for Sn; spectro-
fluorometry and optical emission spectrometry for Be. The
analytical work was performed by T. C. Rains, B. I. Diamondstone,
R. K. Bell, R. A. Velapoldi, and J. L. Weber, Jr.,
all of the Analytical Chemistry Division, National Bureau of
Standards.

4.1 Atomic Absorption Measurements

For atomic absorption, the single filters were solubilized
by transferring a filter to a 100-ml Teflon beaker and adding
5 ml of NBS high purity HNO_3. The filter was digested on a
hot plate until it decomposed (10 minutes), then 2 ml of NBS
high purity $HClO_4$ was added and evaporated to strong fumes.
The solution was cooled, transferred to a 25-ml volumetric
flask and diluted to the calibrated volume. This solution
was used for the determination of Pb, Zn, Cd, and Mn by
conventional techniques [2]. The spectra were excited with
an air-acetylene flame, and measured at the following wavelengths:
Pb at 283.3 nm; Zn at 213.9 nm; Cd at 228.8 nm; Mn at 279.5 nm.

The calibration solutions were prepared by weighing requisite
amounts of the pure metals, dissolution in pure acids, and dilu-
tion with pure water. Experience in the laboratory has shown
that solutions so prepared are accurate to 0.1 percent or
better. The atomic absorption measurement techniques used

7

have been demonstrated to have uncertainties no greater than
± 2 percent.

4.2   Spectrophotometric Measurements

For spectrophotometry, the filters were digested in a
mixture of HNO_3-H_2SO_4. The diluted solution (50 ml) was used
to determine Sn by adding potassium acid phthalate, pyrocatechol
violet and NH_4OH to a suitable aliquot, following the published
procedure [3]. Spectrophotometric measurements were made at
555 nm. The calibration solutions for this procedure were
prepared in a manner similar to that described above. The
spectrophotometric measurements are believed to have an overall
uncertainty of no more than ± 2 percent.

4.3   Spectrofluorometric Measurements

For spectrofluorometry of Be, the following procedure was
used. The analyses were performed using a method by Kirkbright,
et al. [4] with modifications by Christopher and Burke [5].

The filters were placed in 50-ml Teflon beakers, 2 ml
HNO_3 (NBS redistilled) was added, and digested on a hot plate
until decomposed. Then 1.25 ml $HClO_4$ was added to each, and
the solutions were heated and evaporated until copious white
fumes ($HClO_4$) were emitted and ~1 ml of solution remained.
The solutions were transferred quantitatively to appropriately
numbered 100-ml volumetric flasks, 25 ml of water was added,
and the volumetrics were stoppered. To each of the volumetric
flasks, 5 ml Ca(II)/DCTA was added and one drop phenol red,

8

after which the pH was adjusted to ~8.0 with dilute NH_4OH (pH determined by pink color change). Then 5 ml of buffer and 10 ml of (2.22 x 10^{-6} moles) 3-hydroxy-2-naphthoic acid were added. The solutions were diluted to the mark with water, shaken, and measured on a spectrofluorimeter (λ_{ex} = 370 nm, λ_{em} = 460 nm, slits = 20).

Standards containing 0.1, 0.2 and 0.4 µg Be(II) were prepared and run with each series of filters by placing blank filters in 50-ml Teflon beakers, adding 0.1, 0.2 and 0.4 µl of 1 ppm Be solution and carrying out filter dissolution as with the Be-doped samples. A blank was also run by dissolving one non-doped filter in the same manner as the samples and standards. After the 2 filters with ~0.1 µg Be were measured, the 0.1 µg standard solution was fun, followed by the blank. In one case, two blanks were run, one first and one last. Essentially no differences in results were observed, so the former procedure was followed for each concentration of the Be standard.

4.4   Optical Emission Measurements

This procedure was applied to determine Be in the working solutions used to add this element to the filters. Conventional techniques [6] were used in conjunction with capillary cup graphite electrodes and a 2 m direct reading spectrometer. The solutions, with a nominal content of 1; 2; and 4 µg/ml Be were used directly and measured against aqueous standards of Be.

9

5. Analytical Results

The analytical results are summarized in Table 1. The
table indicates the number of filters analyzed (N); the
average assay value; the theoretical or predicted value, based
on solution composition and volume delivered; the standard
deviation of a single measurement (s); and the coefficient of
variation (CV). The standard deviation represents both
analytical uncertainty and variability of sample composition.
The measured and predicted values agree within the measurement
uncertainty except for one case (Zn in 2A, 2B, and 2C). This
is due to an error in preparing the composite solution, which
has been verified by analysis.

It is recommended that the theoretical value be accepted
as the "true" value except for the case of Zn (2A, 2B, and 2C)
where the measured values should be used. The recommended values
are tabulated in Table 2.

It is recommended that the identification number be
clipped from the filter by the analyst at the time of analysis.
It is required that the entire filter be used in the analysis,
since the distribution of the deposit upon the filter is not
predictable.

6. Conclusion

The filters prepared by the techniques described should
be very useful for evaluating analytical methods for toxic metal
analysis. When a given laboratory's results are compared with

10

the recommended values, a difference in slope from 1.00 of
2 percent would be a significant indication of analytical bias.

7. References

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2. "Atomic Absorbtion Spectroscopy", Walter Slavin, Interscience (1968).

3. W. J. Ross and J. C. White, Anal. Chem., 33, 421 (1961).

4. G. F. Kirkbright, T. S. West, and C. Woodward, Anal. Chem. 31, 137 (1965).

5. D. Christopher and R. W. Burke, NBS Tech. Note 454 (1968), and private communication.

6. "Methods for Emission Spectrochemical Analysis", ASTM (1971).

Table 1

Summary of Analytical Data

Group & Metal		N	Assay value	Theoretical value	s μg	%cv
1A	Pb	8	7.49	7.4	0.270	3.60
	Cd	6	4.70	4.9	0.632	1.35
	Zn	5	99.18	99.	1.54	1.56
	Sn	10	142.82	148.	2.63	1.84
1B	Pb	8	15.31	14.8	0.439	2.87
	Cd	6	9.43	9.9	0.121	1.28
	Zn	6	203.28	198.	2.23	1.10
	Sn	10	303.94	297.	3.66	1.20
1C	Pb	8	29.99	29.7	0.449	1.50
	Cd	6	18.38	19.8	0.264	1.44
	Zn	6	409.12	396.	2.46	0.60
	Sn	10	618.00	594.	6.67	1.11
2A	Pb	4	7.45	7.4	0.412	5.53
	Zn	4	111.0	99.	1.41	1.27
	Mn	4	236.25	248.	1.26	0.53
2B	Pb	4	14.45	14.8	0.646	4.47
	Zn	4	226.25	198.	5.32	2.35
	Mn	4	480.75	495.	4.27	0.89
2C	Pb	4	29.425	29.7	0.850	2.89
	Zn	4	452.5	396.	7.05	1.56
	Mn	4	964.75	990.	11.26	1.17
3A	Be	6	0.0993	0.099	0.00258	2.60
3B	Be	6	0.2023	0.198	0.00423	2.09
3C	Be	6	0.4047	0.405	0.00615	1.52

Table 2

Recommended Values for Metal Content of Filters

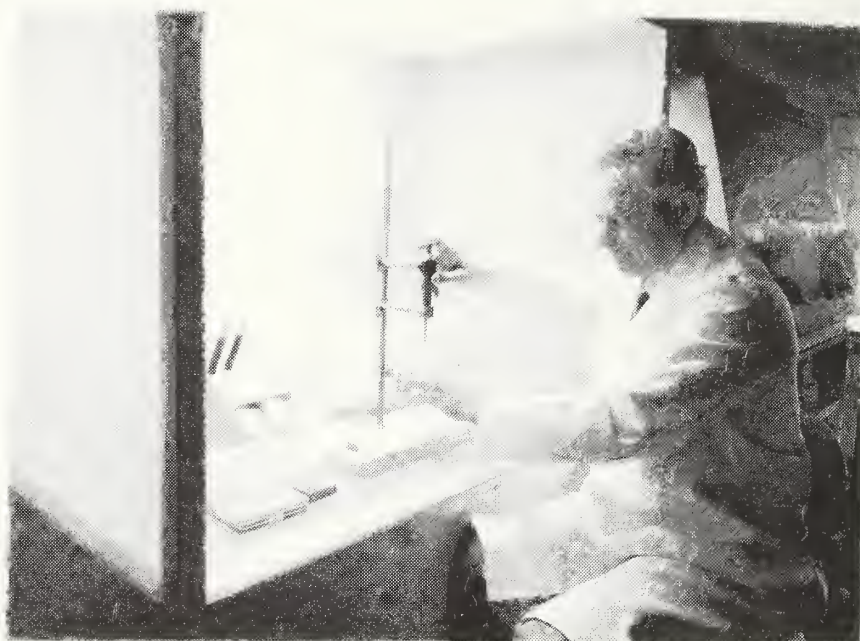|	Pb	Cd	Zn	Sn	Mn	Be
			μg metal/filter			
Set No. 1						
1A	7.4	4.9	99	148	--	--
1B	14.8	9.9	198	297	--	--
1C	29.7	19.8	396	594	--	--
Set No. 2						
2A	7.4	--	111	--	248	--
2B	14.8	--	226	--	495	--
2C	29.7	--	452	--	990	--
Set No. 3						
3A	--	--	--	--	--	0.099
3B	--	--	--	--	--	0.198
3C	--	--	--	--	--	0.396

13

Figure 1. Preparation of the membrane filters with
deposited metals.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

Techniques are described that may be used to prepare filters on which are deposited prescribed amounts of heavy metals, for use as reference materials in industrial atmospheric analysis. Working solutions, prepared from pure metals and highly purified acids and water, are pipetted onto the filters held in jigs to facilitate their application. The techniques were used to prepare three sets of reference materials containing the following metals: Set 1--Pb, Cd, Zn, Sn; Set 2--Pb, Zn, Mn; Set 3--Be. The amounts of each metal deposited on the filters correspond to those expected when collecting personal samples, in atmospheres when the concentrations are both below and above the TLV levels.

17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)

Analysis of toxic materials; atmospheric analysis; industrial hygiene; reference materials.

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